

(19) Europäisches Patentamt
European Patent Office

Office européen des brevets



(11) EP 1 041 189 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
23.06.2004 Bulletin 2004/26

(51) Int Cl.⁷: D06L 1/04

(21) Application number: 00301475.0

(22) Date of filing: 24.02.2000

(54) Dry cleaning composition and process

Zusammensetzung und Verfahren zum Chemischreinigen

Composition et procédé pour la nettoyage à sec

(84) Designated Contracting States:
DE FR GB

• Perry, Robert J.
Niskayuna, New York 12309 (US)

(30) Priority: 31.03.1999 US 282828

(74) Representative: Szary, Anne Catherine, Dr. et al
London Patent Operation
General Electric International, Inc.
15 John Adam Street
London WC2N 6LU (GB)

(43) Date of publication of application:
04.10.2000 Bulletin 2000/40

(56) References cited:

(73) Proprietor: GENERAL ELECTRIC COMPANY
Schenectady, NY 12345 (US)

EP-A- 0 609 456 DE-A- 3 739 711
US-A- 5 676 705 US-A- 6 063 135

(72) Inventors:
• Kilgour, John Alfred
New York 12065 (US)

EP 1 041 189 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] The present invention is directed to a composition, more specifically, to a siloxane fluid based composition, for use in dry cleaning and to a dry cleaning process using the composition.

5 [0002] Current dry cleaning technology uses perchloroethylene ("PERC") or petroleum-based materials as the cleaning solvent. PERC suffers from toxicity and odor issues. The petroleum-based products are not as effective as PERC in cleaning garments.

10 [0003] Cyclic siloxanes have been reported as spot cleaning solutions, see US 4,685,930 and for dry cleaning, see DE 37 39 711. Other patents disclose the use of silicone soaps in petroleum solvents, see JP 09299687, and the use of silicone surfactants in super critical carbon dioxide solutions has been reported, see, for example, US 5,676,705 and Chem. Mark. Rep., 15 Dec 1997, 252(24), p. 15. Non-volatile silicone oils have also been used as the cleaning solvent requiring removal by a second washing with perfluoroalkane to remove the silicone oil, see JP 06327888.

15 [0004] Numerous other patents have issued in which siloxanes or organomodified silicones have been present as addenda in PERC or petroleum based dry cleaning solvents, see, for example, WO 9401510; US 4911853; US 4005231; US 4065258.

[0005] In a first aspect, the present invention is directed to a dry cleaning composition, comprising a cyclic siloxane and a siloxane surfactant.

20 [0006] In a second aspect, the present invention is directed to a method for dry cleaning an article, comprising contacting the article with a composition comprising a cyclic siloxane and a siloxane surfactant.

[0007] The process of the present invention effectively removes both oil soluble and water soluble stains from the article, for example a garment, being cleaned and suppresses redeposition of soil on the article.

25 [0008] In a preferred embodiment, the composition comprises, based on 100 parts by weight ("pbw") of the composition, from 80 pbw to 99.99 pbw, more preferably from 90 pbw to 99.9 pbw and even more preferably from 92 pbw to 99.5 pbw of the cyclic siloxane and from 0.01 pbw to 20 pbw, more preferably from 0.1 pbw to less than 10 pbw and even more preferably from 0.5 pbw to 8 pbw of the siloxane surfactant.

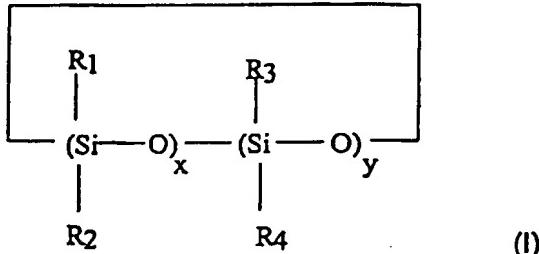
[0009] In a preferred embodiment, the composition further comprises, based on 100 pbw of the composition, up to 10 pbw, more preferably from 0.01 pbw to 10 pbw, even more preferably from 0.1 pbw to 5 pbw, even more preferably 0.5 pbw to 2 pbw water.

30 [0010] Compounds suitable as the cyclic siloxane component of the present invention are those containing a polysiloxane ring structure that includes from 2 to 20 silicon atoms in the ring. Preferably, the cyclic siloxanes are relatively volatile materials, having, for example, a boiling point of below about 250°C at a pressure of 760 millimeters of mercury ("mm Hg").

[0011] In a preferred embodiment, the cyclic siloxane comprises one or more compounds of the structural formula (I):

35

40



45

wherein:

50 R¹, R², R³, R⁴ are each independently a monovalent hydrocarbon group; and x and y are each independently integers from 0 to 10, provided that 3 ≤ (x + y) ≤ 10.

55 [0012] Preferred monovalent hydrocarbon groups are monovalent alkyl groups, monovalent aryl groups and monovalent aralkyl groups, more preferably, the monovalent hydrocarbon group is a monovalent (C₁-C₈)alkyl group, most preferably, methyl.

[0013] As used herein, the term "(C₁-C₈)alkyl" means a linear or branched alkyl group containing from 1 to 6 carbons per group, such as, for example, methyl, ethyl, propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, pentyl, hexyl, preferably methyl.

[0014] As used herein, the term "aryl" means a monovalent unsaturated hydrocarbon ring system containing one or more aromatic rings per group, which may optionally be substituted on the one or more aromatic rings, preferably with one or more (C_1 - C_6)alkyl groups and which, in the case of two or more rings; may be fused rings, including, for example, phenyl, 2,4,6-trimethylphenyl, 2-isopropylmethylphenyl, 1-pentenyl, naphthyl, anthryl, preferably phenyl.

5 [0015] As used herein, the term "aralkyl" means an aryl derivative of an alkyl group, preferably a (C_2 - C_6)alkyl group, wherein the alkyl portion of the aryl derivative may, optionally, be interrupted by an oxygen atom, such as, for example, phenylethyl, phenylpropyl, 2-(1-naphthyl)ethyl, preferably phenylpropyl, phenoxypropyl, biphenyloxypropyl.

10 [0016] In a preferred embodiment, the cyclic siloxane comprises one or more of, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, tetradecamethylcycloheptasiloxane. In a more highly preferred embodiment, the cyclic siloxane of the present invention comprises decamethylcyclopentasiloxane. In a highly preferred embodiment, the cyclic siloxane component of the composition of the present invention consists essentially of decamethylcyclopentasiloxane.

[0017] Suitable cyclic siloxanes are made by known methods, such as, for example, hydrolysis and condensation of dimethylchlorosilane and are commercially available.

15 [0018] In a preferred embodiment, the siloxane surfactant component of the present invention comprises one or more polyether siloxane compounds according to the structural formula II:



20

wherein:

M is $R^5_3SiO_{1/2}$;

25

D is $R^6_2SiO_{2/2}$;

M^* is $R^1_3SiO_{1/2}$;

D^* is $R^8_2SiO_{2/2}$;

30 each R^5, R^6 is independently H, or a monovalent hydrocarbon group,

each R^7 is independently H, a monovalent hydrocarbon group, or $(CH_2)_g-O-(C_2H_4O)_h-(C_3H_6O)_i-(C_nO_{2n}O)_j-R^{11}$, provided that at least one R^7 is $(CH_2)_g-O-(C_2H_4O)_h-(C_3H_6O)_i-(C_nO_{2n}O)_j-R^{11}$;

35 each R^8 is independently H, a monovalent hydrocarbon group, or $(CH_2)_g-O-(C_2H_4O)_h-(C_3H_6O)_i-(C_nO_{2n}O)_j-R^{11}$, provided that at least one R^8 is $-(CH_2)_g-O-(C_2H_4O)_h-(C_3H_6O)_i-(C_nO_{2n}O)_j-R^{11}$;

40 R^{11} is H, a monovalent hydrocarbon group or alkyloxy;

45 $0 \leq a \leq 2$;

$0 \leq e \leq 1000$;

50 $0.1 \leq f \leq 50$;

$1 \leq g \leq 16$;

$0 \leq h \leq 30$;

$0 \leq i \leq 30$;

$0 \leq j \leq 30$; and

55 $4 \leq n \leq 8$

provided that $h + i + j > 0$.

[0019] In a preferred embodiment, $2 \leq h \leq 25$, $0 \leq i \leq 25$ and $0 \leq j \leq 25$, more preferably j is 0.

[0020] The composition of the present invention may optionally contain other components, such as, for example, fabric conditioners, brighteners, water-repellent treatments, anti-static agents, fragrances and detergents, as well as other surfactants in addition to the polyether siloxane component of the present invention. Other surfactants include other silicone-based surfactants, as well as inorganic-based or organic-based surfactants, such as, for example, anionic, nonionic, Zwitterionic and ampholytic surfactant compounds. Such additive compounds are well known in the art and are available from a number of commercial sources.

[0021] In a preferred embodiment, the dry cleaning composition of the present invention further comprises a minor amount, preferably, less than 50 pbw per 100 pbw of the composition, and, more preferably, less than 10 pbw per 100 pbw of the composition, of one or more non-siloxane fluids. Suitable non-siloxane fluids include aqueous fluids, such as, for example, water, and organic fluids, for example, hydrocarbon fluids and halogenated hydrocarbon fluids.

[0022] An article, such as for example, a textile or leather article, typically, a garment, is dry cleaned by contacting the article with the composition of the present invention. In a preferred embodiment, the articles to be cleaned include textiles made from natural fibers, such as for example, cotton, wool, linen and hemp, from synthetic fibers, such as, for example, polyester fibers, polyamide fibers, polypropylene fibers and elastomeric fibers, from blends of natural and synthetic fibers, from natural or synthetic leather or natural or synthetic fur.

[0023] The article and dry cleaning composition are then separated, by, for example, one or more of draining and centrifugation. In a preferred embodiment, separation of the article and dry cleaning composition is followed by the application of heat, preferably, heating to a temperature of from 15 °C to 120 °C, preferably from 20 °C to 100 °C, or reduced pressure, preferably, a pressure of from 1 mm Hg to 750 mm Hg, or by application of heat and reduced pressure, to the article.

[0024] The process removes both water soluble soil, such as for example, salts, sugars, water soluble biological fluids, and oil soluble soils, such as, for example, hydrocarbons, oils, greases, and sebum, from the garment and prevents the redeposition of both oil and water soluble stains on the article.

EXAMPLES 1-56 and COMPARATIVE EXAMPLES C1-C4

[0025] The respective dry cleaning compositions used in Examples 1-56 and Comparative Examples C1-C4 were each prepared by combining decamethylcyclopentasiloxane ("D₅") with a polyether siloxane compound and, in some cases, water, in the relative amounts set forth below in TABLES I - IV below. The following polyether siloxane compounds, each according to structural formula II above, were used:

	Surfactant	a	e	f	Ratio C ₂ H ₄ O: C ₃ H ₆ O	Number average molecular weight (MW _n) of polyether substituent	R ¹¹
35	A	2	20	3	50: 50	1700	H
	B	2	15	5	100: 0	550	H
40	C	0	3	0	100: 0	900	H
	D	0	3	0	100: 0	200	H
45	E	2	500	6.5	50: 50	1700	H
	F	2	400	18	100: 0	550	H

[0026] A first set of textile samples (2" x 2" squares of satin textile) were soiled with water soluble stains by pipetting droplets of an 8 wt % aqueous sodium chloride solution on each of the textile samples of the set. A second set of textile samples were soiled with oil soluble stains by pipetting droplets of fresh motor oil (Quaker State SAE 10W-30) on each of the textile samples of the set. Each of the dry cleaning compositions was deposited in a 4 ounce bottle. Each of the soiled textile samples was contacted with a respective one of the dry cleaning compositions by immersing the soiled textile sample in 50 g of one of the dry cleaning compositions. The textile samples and dry cleaning compositions were agitated by gently shaking each of the bottles. Following agitation, each of the textile samples was removed from the dry cleaning composition, allowed to drain, blotted and then heated at -50°C to dry the samples. The appearance of each of the dried textile samples was then evaluated by visual inspection and rated on the following scale:

EP 1 041 189 B1

5	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 10%;">Rating</td><td style="width: 90%;">5 = complete removal of stain</td></tr> <tr> <td></td><td>4 = slight stain remaining</td></tr> <tr> <td></td><td>3 = moderate stain removal</td></tr> <tr> <td></td><td>2 = slight stain removal</td></tr> <tr> <td></td><td>1 = no stain removal</td></tr> </table>	Rating	5 = complete removal of stain		4 = slight stain remaining		3 = moderate stain removal		2 = slight stain removal		1 = no stain removal
Rating	5 = complete removal of stain										
	4 = slight stain remaining										
	3 = moderate stain removal										
	2 = slight stain removal										
	1 = no stain removal										
10											

[0027] The amounts of D₅, polyether siloxane and water used in each of Examples 1-56 and Comparative Examples C1-C4, the type of stain and the results obtained are set forth in TABLES I-IV below.

TABLE I

Exp #	D ₅ , (g)	Amount Stain	Polyether Siloxane	Polyether Siloxane, Amount (g)	H ₂ O, (g)	Amount Cleaning
C1	49.5	Salt	—	—	—	2.3
1	49.5	Salt	A	0.5	—	3.7
2	49	Salt	A	0.5	0.5	4.7
3	49.5	Salt	F	0.5	—	3.7
4	49	Salt	F	0.5	0.5	3.7
5	49.5	Salt	B	0.5	—	4
6	49	Salt	B	0.5	0.5	4
7	49.5	Salt	C	0.5	—	4.7
8	49	Salt	C	0.5	0.5	4
9	49.5	Salt	D	0.5	—	4
10	49	Salt	D	0.5	0.5	2.7
11	49.5	Salt	E	0.5	—	4.7
12	49	Salt	E	0.5	0.5	4.3
13	49.5	Salt	B/E	0.25/0.25	—	2.7
14	49	Salt	B/E	0.25/0.25	0.5	4

TABLE II

Exp #	D ₅ , (g)	Amount Stain	Polyether Siloxane	Polyether Siloxane, Amount (g)	H ₂ O, (g)	Amount Cleaning
C2	47.5	Salt	—	—	—	2.7

EP 1 041 189 B1

TABLE II (continued)

	Exp #	D ₅ , (g)	Amount Stain	Polyether Siloxane	Polyether Siloxane, Amount (g)	H ₂ O, (g)	Amount Cleaning
5	15	47.5	Salt	A	2.5	—	5
	16	47	Salt	A	2.5	0.5	5
10	17	47.5	Salt	F	2.5	—	3
	18	47	Salt	F	2.5	0.5	4.3
15	19	47.5	Salt	B	2.5	—	5
	20	47	Salt	B	2.5	0.5	5
20	21	47.5	Salt	C	2.5	—	4
	22	47	Salt	C	2.5	0.5	4.7
25	23	47.5	Salt	D	2.5	—	5
	24	47	Salt	D	2.5	0.5	5
30	25	47.5	Salt	E	2.5	—	4.7
	26	47	Salt	E	2.5	0.5	4.7
35	27	47.5	Salt	B/E	1.25/1.25	—	3
	28	47	Salt	B/E	1.25/1.25	0.5	3.7

TABLE III

	Exp #	D ₅ , (g)	Amount Stain	Polyether Siloxane	Polyether Siloxane, Amount (g)	H ₂ O, Amount (g)	Amount Cleaning
40	C3	49.5	Oil	—	—	—	4
	29	49.5	Oil	A	0.5	—	5
45	30	49	Oil	A	0.5	0.5	4
	31	49.5	Oil	F	0.5	—	5
50	32	49	Oil	F	0.5	0.5	5
	33	49.5	Oil	B	0.5	—	4.7
55	34	49	Oil	B	0.5	0.5	3.7

EP 1 041 189 B1

TABLE III (continued)

Exp #	D ₅ , (g)	Amount Stain	Polyether Siloxane	Polyether Siloxane, Amount (g)	H ₂ O, Amount (g)	Amount Cleaning	
5	35	49.5	Oil	C	0.5	—	4
	36	49	Oil	C	0.5	0.5	3
10	37	49.5	Oil	D	0.5	—	3.7
	38	49	Oil	D	0.5	0.5	5
15	39	49.5	Oil	E	0.5	—	5
	40	49	Oil	E	0.5	0.5	5
20	41	49.5	Oil	B/E	0.25/0.25	—	4.7
	42	49	Oil	B/E	0.25/0.25	0.5	5

TABLE IV

Exp #	D ₅ , (g)	Amount Stain	Polyether Siloxane	Polyether Siloxane, Amount (g)	H ₂ O, (g)	Amount Cleaning	
25	C4	47.5	Oil	—	—	4	
	43	47.5	Oil	A	2.5	—	5
30	44	47	Oil	A	2.5	0.5	5
	45	47.5	Oil	F	2.5	—	5
35	46	47	Oil	F	2.5	0.5	5
	47	47.5	Oil	B	2.5	—	5
40	48	47	Oil	B	2.5	0.5	5
	49	47.5	Oil	C	2.5	—	5
45	50	47	Oil	C	2.5	0.5	4
	51	47.5	Oil	D	2.5	—	5
50	52	47	Oil	D	2.5	0.5	5
	53	47.5	Oil	E	2.5	—	5
55	54	47	Oil	E	2.5	0.5	5
	55	47.5	Oil	B/E	1.25/1.25	—	5

TABLE IV (continued)

Exp #	D ₅ , (g)	Amount Stain	Polyether Siloxane	Polyether Siloxane, Amount (g)	H ₂ O, (g)	Amount Cleaning
5 56	47	Oil	B/E	1.25/1.25	0.5	4.5

Claims

- 10 1. A dry cleaning composition, comprising a cyclic siloxane and a siloxane surfactant.
2. A method for dry cleaning an article, comprising contacting the article with a composition comprising a cyclic siloxane and a siloxane surfactant.

Patentansprüche

- 20 1. Zusammensetzung zum chemisch Reinigen umfassend ein zyklisches Siloxan und ein Siloxantensid.
2. Verfahren zum chemischen Reinigen eines Gegenstandes bei welchem man den Gegenstand mit einer Zusam-
- mensetzung in Berührung bringt, die ein zyklisches Siloxan und ein Siloxantensid umfasst.

Revendications

- 25 1. Composition de nettoyage à sec, comprenant un siloxane cyclique et un tensioactif de type siloxane.
2. Procédé de nettoyage à sec d'un article, comportant le fait de mettre cet article en contact avec une composition comprenant un siloxane cyclique et un tensioactif de type siloxane.

35

40

45

50

55